

The University of Chicago

REACTION AND COMPOUNDS OF
THE $(\text{CH}_3)_2\text{B-}$ GROUP

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By

FORREST LEE McKENNON

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REACTION AND COMPOUNDS OF THE $(\text{CH}_3)_2\text{B-}$ GROUP

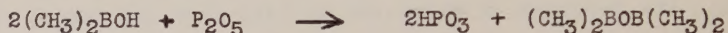
In connection with the study of the hitherto discovered hydrides of boron, all of which, like diborane, exhibit abnormal valence relation, it is important to search for evidence of the existence of hydrides such as monoborine, BH_3 , and diborine, B_2H_4 , the formulae of which are derived from the normal valence of boron, as the formulae of the saturated hydrocarbons are derivable from the quadrivalence of carbon. The fact that such compounds have not yet been discovered¹ indicates that the hydrides themselves are very unstable, and that their study should be approached through that of the more stable derivatives and analogues. Of monoborine numerous derivatives, such as boron trimethyl $\text{B}(\text{CH}_3)_3$ and dimethoxyborine $(\text{CH}_3\text{O})_2\text{BH}$, are known and readily available for study. Of diborine no derivatives are known.² It seemed desirable therefore to study radicals of the type BR_2 in order to gain some understanding of the factors which seem to prevent the union of these radicals to form the desired B_2R_4 molecules. For this purpose the present investigation of compounds containing the $\text{B}(\text{CH})_2$ radical, and the comparison of these compounds with the corresponding carbon derivatives was undertaken. This comparison shows that compounds containing the radical in question are very different from those containing alkyl radicals, and that a thorough understanding of these differences is necessary

¹Recently Schlesinger and Burg (unpublished results) have obtained compounds of the molecular formulae BH_3CO and $\text{BH}_3\text{N}(\text{CH}_3)_3$ respectively.

²The compound B_2Cl_4 (Stock, Brandt, and Fischer, Ber., 58 643 (1925)) is a possible exception. It is difficult to prepare and very unstable, and very little is known about it.

before success can attend efforts at preparing diborine derivatives.

Some of these differences are, of course, already known. For example, dimethylboric acid, $B(CH_3)_2OH$, as its name implies, is comparable to an organic acid rather than to an alcohol. Similarly, its anhydride is much more like the anhydride of an acid than like an ether. It is obtained, as will be described later, by the action of phosphorus pentoxide on dimethylboric acid:



Unlike true ethers, the anhydride is readily hydrolyzed and is not acted on by hydrogen halides such as hydrogen iodide.

The same contrast is shown by the reaction of dimethylboric acid with boron trichloride. The latter reacts with alcohols to form stable trialkyl borates¹ which show little tendency toward ether formation. With dimethylboric acid, on the other hand, boron trichloride reacts to form only dimethylboric anhydride and a solid, the composition of which approximates $(CH_3)_2BOBO$. It appears that any substance, such as $((CH_3)_2BO)_3B$, an analogue of a trialkyl borate, is too unstable to be obtained at room temperature.

Another sharp difference between dimethyl boric acid and alcohols is shown by the reaction of each with diborane. Methyl alcohol and diborane, for example, react very rapidly with evolution of hydrogen² and formation of dimethoxyborine; the main reaction³ of dimethyl boric acid, as well as of its anhydride, with

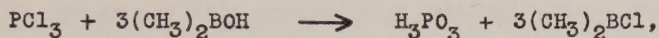
¹Wiberg and Sutterlin, Z. anorg. allgem. Chem., 202, 31 (1931).

²See J. Am. Chem. Soc., 55, 4020 (1933).

³In the earlier stages of the reaction of diborane with dimethylboric acid, a solid and a small amount of hydrogen were produced. The reaction of diborane with dimethylboric anhydride differs in this respect. However, in the latter stages, the reactions are similar in that a solid and the methyl derivatives appear.

diborane is one of slow methylation similar to that which occurs in the action of borontrimethyl on diborane.

Of particular interest for a study of the $B(CH_3)_2$ group are the corresponding halides, $B(CH_3)_2X$, for the preparation of which no very satisfactory methods seem hitherto to have been available. Two reactions seemed feasible as a means of obtaining dimethyl boron chloride - the reaction of phosphorus trichloride on trimethylboric acid:

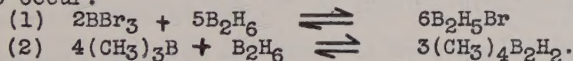


and the reaction of boron trimethyl on boron trichloride:



Both because of the reversibility of the latter reaction and of the fact that separation of boron trimethyl, boron trichloride and dimethylboron chloride by fractional distillation is very difficult, these reactions did not lead to the actual isolation of the desired compound, although its presence could readily be demonstrated in the reaction mixture. In fact, hydrolysis of mixtures of boron trichloride and boron trimethyl, which had been allowed to stand at room temperature for several hours, yielded an amount of dimethyl boric acid corresponding to a 90 per cent yield of dimethyl boron chloride. This finding led at once to a study of the reaction between boron trimethyl and boron bromide. Equilibrium in this case is attained very slowly at room temperature, but may be reached in a few hours at the temperature of a steam bath, if a trace of diborane is used as a catalyst.¹ The

¹A possible explanation of the catalytic effect of the diborane is seen in the following equations for reactions which are known to occur:



Substitution of bromine for hydrogen in tetramethyl diborane by a reaction of type (1) would lead to an unstable molecule which would decompose to dimethyl boron bromide.

slowness with which equilibrium is established at lower temperatures, and the more favorable distillation conditions make isolation of the dimethyl boron bromide possible.

With this substance available, a study of reactions analogous to a Würtz synthesis in organic chemistry could be undertaken. Here again the difference between the radical $B(CH_3)_2$ and alkyl radicals was displayed. When dimethyl boron bromide was treated in turn with sodium, lithium, mercury, tin, zinc, magnesium, copper and sodium amalgam, no reaction with the metals occurred. The slight change which took place appeared to be due to the disproportionation of dimethylboron bromide into boron trimethyl and boron tribromide, and the reaction of the latter with the metal to give boron alloys.

A number of variants of the reaction were carried out. Since alkyl iodides are often more reactive toward certain metals, dimethyl boron iodide was prepared by action of hydrogen iodide on boron trimethyl, and its reactions with metals investigated. The results were essentially like those observed with the corresponding bromide. Next, attempts were made to induce the reaction by the use of solvents, as is often done in carrying out Würtz syntheses. The solvents chosen were dibutyl ether and trimethylamine. An ether was desired because of the known tendency of such substances to form addition products with boron compounds, and dibutyl ether was selected because more volatile ethers would have been difficult to separate from the reacting substances or from the expected reaction products. Trimethylamine was chosen because reports in the literature indicated that at least one metal, lithium, is appreciably soluble in it, and because it, as a polar substance, might be expected to favor the reaction sought.¹

¹Ammonia unfortunately cannot be used because it acts on the boron halides.

Apparently, however, lithium is soluble in trimethylamine only if the latter is contaminated with dimethylamine; once dimethylamine is removed from the solvent by action with dimethyl boron bromide, lithium ceases to dissolve. Neither the use of dibutyl ether nor of trimethylamine led to reaction between dimethyl boron bromide and metals.¹

Finally, one other attempt to prepare new derivatives of borine and of diborine should be described briefly. The reaction of diborane with carbon monoxide has recently been shown to lead to the formation of a compound of the molecular formula, BH_3CO .² Should carbon monoxide react in similar fashion with tetramethyl diborane, a method for obtaining dimethylborine might have been made available. But the reaction of tetramethyl diborane with carbon monoxide follows a course entirely different from that of diborane and carbon monoxide. Instead of an analogue of the unstable BH_3CO , the reaction led to the formation of a number of relatively stable substances, some of which seem to be obtained from the other by reversible reactions. Only one of these was isolated. Its composition and molecular weight agreed with the formula, $((\text{CH}_3)_2\text{HBCO})_2$. The substance seems to contain neither B-B nor B-H linkages for no hydrogen is liberated by hydrolytic reactions even though carried out under very drastic conditions. Nevertheless, the production of the compounds is related to a B-H linkage in the source material, since boron halides, boron trimethyl, and dimethyl boron bromide and iodide all failed to react with carbon monoxide. The reaction requires further study.

¹Both dibutyl ether and trimethylamine were shown to form compounds with dimethyl boron bromide. The compound with trimethylamine is relatively very stable, far more so, for example, than the compound $\text{B}(\text{CH}_3)_3\text{NH}_3$.

²Unpublished work of Schlesinger and Burg.

Experimental¹

1. Dimethylboric anhydride.— The completeness with which dimethyl boric acid at ordinary temperatures is converted by phosphorus pentoxide into the anhydride may be seen from the results of two experiments, tabulated below:

<u>Sample</u>	<u>(CH₃)₂BOB(CH₃)₂ Calc.</u>	<u>(CH₃)₂BOB(CH₃)₂ Found</u>
20.4 cc.	12.2 cc.	12.3 cc.
10.6	5.3	5.4

The melting point of the resulting dimethylboric anhydride was measured as -37.2_9° , and -37.4_7° ; average value -37.3° . The measurement of the vapor tensions at temperatures between -21.3° and 5.0° gave data in fair agreement with the Clapeyron equation $\log p = 8.020 - 1625/T$, as indicated in Table I. Calculations

TABLE I

<u>t, °C., obsd.</u>	<u>V. t., mm. obsd.</u>	<u>V. t., mm. calc.</u>
-21.3°	37.0	36.9
-15.0°	53.0	53.0
- 9.0°	73.0	73.6
- 5.0°	92.0	94.0
0.0°	119.0	118.0
5.0°	147.0	150.0

from the equation gives 7260 cal for the molar heat of vaporization, and 23.0 for the Trouton constant. The normal boiling point is estimated to be approximately 43° .

The actual vapor densities of the dimethylboric anhydride showed good agreement with the calculated molecular weight, as shown in Table II.

Two samples of this material were then analyzed by hydrolysis; the observed volumes of dimethylboric acid are compared with

¹The apparatus and the technical methods used in this work were essentially the same as those described by Stock and Somieski and modified by Schlesinger, Burg and their co-workers.

TABLE II

Sample	Weight	Mol. Weight	Mol. Wt. Calc. for (CH ₃) ₂ BOB(CH ₃) ₂
4.14 cc.	0.0180 g.	97.7 g.	97.69 g.
10.40	0.0450	97.0	97.69

those calculated from the equation:



The results are given below:

Sample	(CH ₃) ₂ BOH Calc.	(CH ₃) ₂ BOH Found
10.50 cc.	5.25 cc.	5.26 cc.
12.64	6.32	6.24

2. Reaction of dimethylboric acid with boron trichloride.-

A mixture of 8.8 cc. of boron trichloride and 28.8 cc. of dimethylboric acid was allowed to react for two hours at room temperature. A solid unidentified product, 10.2 cc. of dimethylboric anhydride, and 26.8 cc. of hydrogen chloride were produced.

3. Reaction of phosphorus trichloride with dimethylboric acid.- This reaction is rapid at room temperature, producing phosphorus acid, hydrogen chloride, boron trimethyl, boron trichloride and a fraction, intermediate in volatility between boron trichloride and boron trimethyl. This intermediate material exhibited a vapor tension of 24 mm. at -80° and behaved in all other respects in much the same manner as the reaction mixture of boron trichloride and boron trimethyl described in the following section.

4. Reaction of boron trichloride with boron trimethyl.-

A mixture of 47.5 cc. of boron trimethyl and 23.8 cc. of boron trichloride was allowed to react for twenty-four hours at room temperature. The mixture, which now showed a vapor tension of 21 mm. at -80°, was next treated with 0.06 cc. of liquid water, which was allowed to react for twelve hours. The investigation

of the products showed that the quantity of water was sufficient for hydrolysis of all the B-Cl bonds present in the sample, but not sufficient to avoid the formation of dimethylboric anhydride, which cannot be separated completely from dimethylboric acid. For this reason, the quantity of $(\text{CH}_3)_2\text{BCl}$ resulting from the original reaction was estimated only roughly.

The results are as follows: $(\text{CH}_3)_2\text{BOH}$, 49 cc.; $(\text{CH}_3)\text{BOB}(\text{CH}_3)_2$, 8 cc.; $(\text{CH}_3)_3\text{B}$, 4.0 cc.; HCl , 69.0 cc.

From these results it is estimated that the reaction $2(\text{CH}_3)_3\text{B} + \text{BCl}_3 \rightleftharpoons (\text{CH}_3)_2\text{BCl}$ was about 90 per cent complete.

5. Dimethyl boron bromide.-- Yields of dimethyl boron bromide as high as 85 per cent are obtained by heating (in a 250 cc. sealed bulb) a mixture of 78.2 cc. of boron tribromide, 154.2 cc. of boron trimethyl and 0.2 cc. of diborane for four hours in a steam bath. The reaction does not occur appreciably at room temperature, nor in the absence of diborane at the higher temperature, even though the duration of heating is doubled.

Dimethyl boron bromide can be prepared also by the action of hydrogen bromide on boron trimethyl at 200° , according to the equation,



A mixture of 63.9 cc. of boron trimethyl and 63.0 cc. of hydrogen bromide, contained in a sealed 250 cc. bulb, was heated four hours in an oil bath at $200\text{--}220^\circ$. The bulb was opened and the incompletely condensable gas, which was passed through a trap at -196° and collected over mercury in a Topley-pump system, was measured as 62.5 cc. and identified as pure methane by its vapor tension at -196° . The material which passed through a U-tube at -112° was found to consist of 4.3 cc. of boron trimethyl and 5.4 cc. of

hydrogen bromide, which remained in spite of the drastic heating.

Dimethyl boron bromide from both reactions was purified by passing it slowly through a U-tube at -90° and trapping it at -112° . The less volatile material, which in the latter experiment amounted to 1.5 cc., was not identified.

The melting point of dimethyl boron bromide was measured as -123.5° , -123.4° , and -123.4° ; average value -123.4° . The measurement of the vapor tensions at temperatures between -57.1° and 15.3° gave data in good agreement with the Clapeyron equation $\log p = 7.692 - 1457/T$, as indicated in the following table:

TABLE III
VAPOR TENSIONS OF $(\text{CH}_3)_2\text{BBr}$

Temp. $^{\circ}\text{C}$.	P.mm.Calc.	P.mm.Obsd.	Temp. $^{\circ}\text{C}$.	P.mm.Calc.	P.mm.Obsd.
-57.1	8.8	8.0	- 7.0	164.6	164.0
-51.6	13.0	12.0	- 5.0	180.9	180.0
-45.4	19.6	18.5	- 3.0	198.3	197.0
-41.4	25.3	24.5	0.0	227.5	228.0
-36.5	34.2	35.0	5.1	285.1	286.0
-31.8	45.1	44.0	10.2	354.0	354.0
-26.7	60.1	61.0	15.3	436.5	434.0
-16.0	106.0	109.0			

Calculations from the equation gives 6660 cal. for the molar heat of vaporization and 22.0 for the Trouton constant. The normal boiling point is estimated to be approximately 22° . Determination of the molecular weight gave the values 122.1 and 119.9 (theoretical 120.8).

A sample of the dimethyl boron bromide was analyzed by hydrolysis. It was found to react with water rapidly and completely at room temperature. The resulting mixture, hydrogen bromide, dimethylboric acid and excess water, was incapable of separation due to the affinity of water for the hydrogen halide. Treatment of this mixture with phosphorus pentoxide removes the

excess water and converts the dimethylboric acid into the anhydride. These latter two compounds are easily separable. The observed volumes of dimethylboric anhydride and hydrogen bromide are compared with those calculated from the equations:

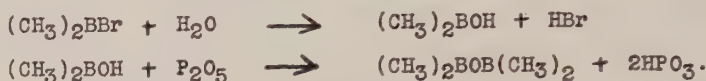


TABLE IV

Sample	HBr Calc.	HBr Found	$(\text{CH}_3)_2\text{BOB}(\text{CH}_3)_2$ Calculated	$(\text{CH}_3)_2\text{BOB}(\text{CH}_3)_2$ Found
10.94 cc. 6.13	10.94 cc. 6.13	11.15 cc. 6.09	5.47 cc. 3.06	5.43 cc. 3.02

6. Dimethyl boron iodide.- Dimethyl boron iodide was prepared by a method analogous to the second method of preparing dimethyl boron bromide - the action of hydrogen iodide upon boron trimethyl. A mixture of 50 - 60 cc. of hydrogen iodide with 83.7 cc. of boron trimethyl was heated in a closed bulb for four hours at 200° , and the products and residual reactants separated in the same manner as in the analogous experiment. There was produced 56 cc. of methane, 55.4 cc. of dimethyl boron iodide, and possible small traces of less volatile material. There remained 27.9 cc. of unused boron trimethyl.

The dimethyl boron iodide was purified by passing through a U-tube at -80° and trapping completely at -90° . The melting point was measured as -110.7° , -110.8° , and -110.7° ; average value -110.7° . The measurement of the vapor tensions at temperatures between -72.9° and 20.6° gave data in good agreement with the Clapeyron equation $\log p = 7620 - 1600/T$, as indicated in the table on page 11. Calculation from the equation gives 7313 cal. for the molar heat of vaporization, and 21.7 for the Trouton constant. The normal boiling point is estimated to be approximately

65°. Determinations of the molecular weight (theoretical 167.8) gave the values 166.3 and 165.7; average value 166.0. A sample of this material (6.4 cc.) was analyzed by the hydrolysis method employed in the identification of dimethyl boron bromide. This sample of dimethyl boron iodide produced 3.2 cc. of dimethylboric anhydride (theoretical 3.24 cc.).

TABLE V

Temp.°C.	P.mm.Calc.	P.mm.Obsd.	Temp.°C.	P.mm.Calc.	P.mm.Obsd.
-57.3	2.4	2.0	- 9.0	36.4	35.0
-47.4	3.4	3.5	- 7.0	40.5	39.5
-44.0	4.3	5.0	- 5.0	44.9	45.0
-31.9	9.7	10.0	0.0	57.7	58.0
-22.4	17.3	17.0	6.2	77.9	78.0
-17.0	23.6	23.0	11.5	98.2	99.0
-14.8	26.7	26.0	15.0	116.4	116.0
-13.0	29.4	29.0	20.6	148.0	147.0

7. Apparent solubility of lithium in trimethylamine.-

Lithium was added to one arm of a V-tube which contained a small quantity of trimethylamine purified by drying over lithium followed by careful fractional distillation. The quantity of lithium used was such that an excess of the metal remained in contact with the blue solution obtained. The other arm of the V-tube contained a small quantity of dimethyl boron bromide. The lithium solution was now poured into the latter. The excess of trimethylamine was distilled back into the tube containing the remainder of the solid lithium, of which none appeared to dissolve as the trimethylamine condensed on it. Evidently the dimethyl boron bromide had removed a trace of impurity which had been responsible for the apparent solubility of lithium in the trimethylamine. The most likely impurity is dimethylamine. The experiments were, of course, carried out under strictly anhydrous conditions.

8. The reaction of tetramethyldiborane with carbon monoxide.- A number of experiments, in which tetramethyldiborane

and carbon monoxide, in various relative and absolute concentrations, were heated together for different periods of time at 100° , all led to the same set of products: a series of compounds which seemed to be chemically related to each other,¹ along with small quantities of the usual products of the disproportionation of tetramethyldiborane.²

The maximum yields of the new material came only by the use of high relative concentrations of carbon monoxide, and total pressures in the neighborhood of five atmospheres. Higher pressures proved to be of no advantage. Boron trimethyl, which was used in some experiments to suppress the disproportionation of tetramethyldiborane, had but little effect upon the total yield, but it seemed to affect the relative quantities of the different products. The longest heating time was thirty minutes; times as short as four minutes were found to be inadequate, but eight minutes was sufficient for a maximum yield.

The new series of compounds was easily freed from the more volatile products of the disproportionation of tetramethyldiborane, by passing the latter through a U-tube at -80° , but the separation of the different members of the series was a matter of far greater difficulty. The only component which was definitely isolated, in a nearly pure condition, was a substance having a vapor tension of 7.1 mm. at 21° . The first samples of this compound contained another material having nearly the same volatility. This material decomposed rather easily (especially at elevated temperatures) to

¹The products were recognized as similar by the following items of evidence: (1) Their aqueous solutions had the same characteristic odor. (2) Their behavior toward water showed the absence of the B-H linkage, and in some cases the absence of B-B linkage was proved also. (3) The action of boron trimethyl upon the most volatile of these substances produced material indistinguishable from the less volatile products of the original reaction.

²Schlesinger and Walker, J. Am. Chem. Soc., 57, 621 (1935).

form substances more and less volatile than itself.¹ While it was thus possible to isolate the more stable substance, by a process of heating and subsequent fractional condensation, the separation was so difficult that an estimation of the yield in any experiment could not be made very satisfactorily. In spite of this difficulty, it is believed that the conditions of the experiment described below represent the best method yet found for obtaining a good yield of the isolable substance.

Tetramethyldiborane (26.0 cc.) and carbon monoxide (247.7 cc.) were condensed into a bomb-tube having a capacity of 87 cc. To insure thorough mixing of the reactants, the sealed-off tube was inverted several times and allowed to stand for one hour at room temperature. The bomb was then heated thirty minutes in a steam bath at 100°. The products were separated into the following fractions:

Hydrogen (by combustion in vacuo).	1 cc., approx.
Carbon monoxide.	203 cc.
Boron trimethyl.	3.5cc.
Dimethyldiborane	0.1cc., approx.
Trimethyldiborane.	0.8cc.
Tetramethyldiborane.	1.3cc.
Most volatile unknown material	4.65cc.
Isolable material.	16.0cc.
(possibly containing unstable substances)	
Less volatile material	0.8cc.

The main product was then heated for thirty minutes in a closed bulb, and then purified by fractional condensation. It was found to pass very slowly through a U-tube at -30°, and was trapped out

¹It is at present not possible to say that the isolable material was a direct product of the original reaction, rather than a secondary product derived from this unstable material.

completely at -35° .

As a test of uniformity, the vapor tensions of this substance were measured at four different temperatures, by the aid of the device shown in Figure 1.¹

The actual pressures and those calculated by the equation $\log_{10} p_{\text{mm}} = 7.203 - 1860/T$ are shown in Table VI.

TABLE VI

Temperature	Pressure (mm.)	Pressure (calc.)
21.0°	7.1	7.5
32.0°	13.2	12.7
41.0°	19.0	19.1
51.5°	29.7	29.6

According to this equation the boiling point is 157° C. and the Trouton constant 19.8 cal./deg. Too much reliance must not be placed on the agreement between observed vapor tensions and the Clapeyron Clausius equation because the temperature range is relatively small. The homogeneity of the material could, furthermore, not be tested by sharpness of the melting point, because the substance solidifies to a glassy solid. For analysis two procedures were employed.

Analysis of $((\text{CH}_3)_2\text{BHC}\text{O})_2$ by oxidation.- Samples of the isolable product of the reaction of tetramethyldiborane with carbon monoxide were burned with oxygen under two different sets of conditions. In both cases the carbon dioxide produced was separated from the volatile products by fractional condensation and measured as a gas, and the boron was determined as boric acid by titration.

¹The sample was condensed into the tubulature of the bulb, and the mercury was allowed to rise into the U-tube leading to the vacuum apparatus. The device was then immersed in water at various elevated temperatures, and the vapor tensions read by means of a cathetometer. After the measurements, the mercury was lowered to the point M (by the aid of a pump attached at (P)), and the sample returned to the vacuum apparatus. The same device was employed for measuring sample volumes for analysis.

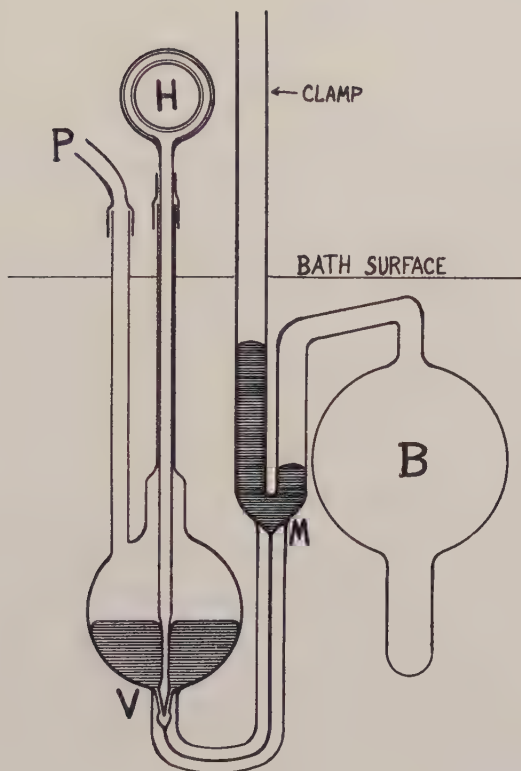


Fig. 1.

It was difficult to determine hydrogen accurately, because a part of it always remained with the boron as boric acid. In analyses by the first method, nitric oxide was used as a catalyst by whose aid the combustion could be completed at a temperature as low as 375°, and the resulting nitric acid was reduced to water and nitric oxide by passage through a tube containing hot copper.¹ It was not found possible to obtain good analyses for hydrogen by this method, mainly because of the great difficulty of estimating the quantity of this element in the boric acid, but the results for carbon and boron were quite satisfactory.

In the second method, combustion was carried out at a higher temperature (500°), and the formation of orthoboric acid was prevented by sudden condensation of the hot vapors into the tubulature of the bulb at -196°. The free water was measured as a gas in the device represented in Figure 1. The residue was heated at 250° with silicon tetrachloride in order to convert the hydrogen retained as metaboric acid into hydrogen chloride. This second method has the disadvantage of giving high results for boron, evidently because of the action of water upon Pyrex glass at the temperatures employed. The values for carbon and boron used for the determination of the formula of the compound were, therefore, those obtained by the first method, those for hydrogen were obtained by the second method.

The analytical results follow:

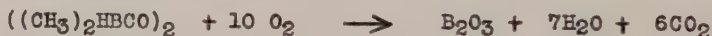


TABLE VII

Method	Vol. of Sample	Vol. of H ₂ O (cc. gas)	Vol. of HCl (cc. gas)	Vol. of Hydrogen (atoms)	Boron (cc. gas)	Vol. of CO ₂ (cc. gas)
First	5.2 cc.	-	64.7	64.7 Found 72.8 Calc.	10.45 F. 10.40 C.	31.4 Found 31.2 Calc.

¹Schlesinger and Walker, op. cit.

TABLE VII--CONTINUED

Method	Vol. of Sample	Vol. of H ₂ O (cc. gas)	Vol. of HCl (cc. gas)	Vol. of Hydrogen (atoms)	Boron (cc. gas)	Vol. of CO ₂ (cc. gas)
Second	4.66cc.	30.0	4.20	64.20 Found 65.24 Calc.	-	27.4 Found 27.9 Calc.

TABLE VIII

MOLECULAR WEIGHT OF ((CH₃)₂HBCO)₂

Sample	Weight	Mol. Weight	Mol. Wt. Calc. for ((CH ₃) ₂ HBCO) ₂
10.94 cc.	0.0899 g.	139.5	139.6
5.15	0.0319	138.8	139.6

The analytical results, together with the molecular weight, give the formula ((CH₃)₂HBCO)₂.

Summary

1. Dimethylboric anhydride ((CH₃)₂BOB(CH₃)₂) was easily prepared from dimethylboric acid by the dehydrating action of phosphorus pentoxide. The reverse reaction occurred very easily when the anhydride was treated with water. Dimethylboric anhydride was produced also by the action of boron trichloride or diborane upon dimethylboric acid. In the latter case it was found that dimethylboric anhydride is a methylating agent for diborane.

2. The dimethyl boron halides (CH₃)₂BCl, (CH₃)₂BBr, and (CH₃)₂BI have been prepared by several methods. The chloride was not isolated, but its presence in the reaction mixtures was shown by the results of hydrolysis. The bromide and iodide, which are more stable than the chloride, were isolated and characterized. All of these methyl boron halides disproportionate into equilibrium mixtures containing boron trimethyl and the corresponding boron halide. Attempts to prepare the hypothetical compound

$\text{B}_2(\text{CH}_3)_4$ from these compounds by the Würtz method proved fruitless.

3. Carbon monoxide was found to react with tetramethyldiborane to form a series of stable compounds, one of which was isolated and found to have the molecular formula $((\text{CH}_3)_2\text{HBCO})_2$.

